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APPLICATION OF COLLOID CHEMISTRY TO STUDY OF FILTER EFFLUENTS¹

BY MALCOLM PIRNIE²

The well known reactions of true solutions fail utterly to explain many phenomena that have been observed in the various processes of water purification. In colloid chemistry, however, we have a collection of relatively new facts demonstrated by a great number of carefully conducted experiments and several theories developed from chains of evidence in given fields of research that are plausible explanations of the observed phenomena. As we have failed, by the simple reactions of inorganic chemistry, to explain most of the phenomena encountered in the purification of natural waters, we may gain new light on our problems by studying the data and theories of colloid chemistry. If the data are analogous and the theories remain plausible, when applied to water treatment, new methods of experimentation will be suggested which will either prove or modify the theories. Such investigations are sure to lead to higher standards of purity for our water supplies.

In order to point out the bearing that colloid chemistry may have upon the study of water purification it will be well to outline briefly a few facts and theories brought out in this special chemical field that seem to be related to recorded phenomena in water purification.

SELECTED FACTS FROM APPLIED COLLOID CHEMISTRY³

Sols, suspensoids and emulsoids

Particles small enough to be in Brownian motion will remain in suspension in a liquid indefinitely if coalescence and resulting agglomeration are prevented. Such particles are called colloids and the liquid and colloids together are called a sol. When the colloidal

¹ Read before the Chemical and Bacteriological Section at the Cleveland Convention, June 9, 1921.

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³ Bancroft, Applied Colloid Chemistry. Hatschek, An Introduction to the Physics and Chemistry of Colloids.

particles agglomerate and precipitate, the precipitate is called a gel. Hydrous alumina and hydrous ferric oxide, when precipitated cold are typical gelatinous precipitates.

Sols of the metals show little or no increase in viscosity for increased concentrations while the organic colloids show marked increase in viscosity even for small increases in concentrations. The metallic colloids are in the form of minute solid particles, while the organic colloids are mostly in the form of minute drops of liquid dispersed in a liquid. Ostwald called the former *suspensoids* and the latter *emulsoids* and these classifications should be useful in differentiating between the treatment of turbid and colored waters. The first would involve the study of suspensoids only; the second, the study of emulsoids; of both emulsoids and suspensoids when coagulant is used.

Adsorption

Careful measurements have been made of the attractive forces (adsorption) exerted between some solids and liquids. Adsorption between solids and liquids has been found to be positive in some cases and negative or repellent in other cases and to be greater between a given solid and one liquid than between the same solid and another liquid. If two liquids have access, therefore, to the same solid the one which is adsorbed most strongly by the solid will surround and wet it. If the strongly adsorbed liquid is introduced in the presence of a weakly adsorbed liquid the latter will be displaced by the former. This is called selective adsorption.

Solids may adsorb substances from solution. This has been demonstrated experimentally by the adsorption of arsenic acid by charcoal and hydrous aluminum oxide and, in a more familiar manner, by the adsorption of sodium hydrate by cotton or filter paper. Lloyd's reagent is a hydrous aluminum silicate which adsorbs alkalis.

Under specific adsorption it has been noted that all salts show distinct adsorption for their own ions. Silver bromide adsorbs silver nitrate and potassium bromide but not potassium nitrate and alumina takes up many acid dyes readily and not the basic dyes.

Adsorption affords an opportunity for chemical action to take place and there is a possibility of chemical decomposition as a result of adsorption. Any acid will tend to react with adsorbed caustic soda the tendency being greater the stronger the acid. Thus a neutral solution will become acid if shaken with a substance that

adsorbs the base more strongly than the acid and alkaline with a substance that adsorbs the acid more strongly than the base.

Adsorption from solution by a liquid has been demonstrated by interesting experiments but, in this case, there is the possibility of the solute dissolving in the second liquid.

Experiments with gelatine and chromic sulphate were carried out to determine whether the gelatine took up the sulphate as a whole or only the chromic oxide. The ratio of chromium to sulphate in the solution was determined before and after sheets of gelatine were immersed in it and found to be practically the same. This demonstrated that the chrome alum is taken up as a whole by gelatine.

In studying the precipitating powers of aluminum sulphate on a negatively charged colloidal solution of mastic the results obtained were first considered abnormal but they have been explained. No precipitation occurred for the first increasing concentrations of aluminum sulphate and the suspension remained negatively charged because the mastic was present in excess. When the concentration of alum became high enough to cause electrical neutrality complete precipitation took place. Higher concentrations caused the mastic to be held in suspension by the hydrolyzed alumina whereupon it was charged positively. At still higher concentrations of aluminum sulphate electrical neutrality was again reached with precipitation. The aluminum sulphate hydrolyzed to colloidal alumina and sulphuric acid with some unchanged aluminum sulphate at the higher concentrations. The free sulphuric acid is equivalent to the amount of alumina so the two concentrations increased proportionally. The second precipitation was caused by the sulphate ions and therefore was normal.

It has been shown that certain sols of like electric charge do not precipitate each other and that certain positive sols when added to certain negative sols to produce electrical neutrality do precipitate each other. This cannot be claimed as proof that sols of the same electrical charge have no effect upon each other because adsorption is not limited to colloids or electrolytes having opposite signs. Thus adsorption may take place between certain colloids of like sign.

Hydrous chromic oxide is peptized by caustic potash and hydrous ferric oxide is not. (Peptization is the reverse of agglomeration.) If the ferric oxide is present in low concentrations relative to the chromium salt, the ferric oxide will adsorb the peptized chromic oxide and be peptized by it forming a colloidal solution. If the ferric oxide

is in excess it will adsorb the peptized chromic oxide and carry it out of the liquid phase. This is a case where chromic oxide when present in excess acts as a protective colloid to the iron oxide. Gelatine protects ferric oxide from precipitation by ammonia when added before the ammonia but a colloidal ferric oxide is precipitated by ammoniacal gelatine. As a matter of fact, many authorities hold that the electric charge on particles is due to adsorbed ions and that coagulation by electrolytes is an adsorption phenomenon.

Bechhold's assumption

The action of the protecting colloids in protecting suspensoids from precipitation by electrolytes can be best explained if we accept Bechhold's assumption that each particle of the suspensoid surrounds itself with a layer of the adsorbed emulsoid or more rarely another suspensoid and then possesses the electrical properties of the latter.

It must be borne in mind that this assumption has not been proved to be a fact although most if not all of the observed actions of protective colloids can be logically explained by adopting it. If it is true it may have a field of application to many problems of sanitation and thereby become of great importance in the study of water purification and sewage disposal.

Protective colloids

It has been known for many years and used extensively in industrial chemistry and the preparation of colloidal solutions that the addition of very small amounts of colloids belonging to the emulsoid groups greatly increase the stability of sols. Such stabilized sols require very much larger amounts of electrolytes for precipitation than do pure suspensoids. Thus colloidal solutions which stabilize the suspensoids are called protective colloids and nearly all of them belong to the emulsoid group. Most of the stable colloidal solutions depend upon the presence of a protecting colloid for their stability. The protective action of various emulsoids on given suspensoids varies considerably and this has been studied by Zsigmondy who determined the quantities of several emulsoids just necessary to protect a definite volume of a standard gold sol from coagulation by a given quantity of sodium chloride. He called this the "gold value" or "gold figure" of the colloid.

It has been shown experimentally that certain solutions will peptize or disintegrate certain precipitates and this is the result of

adsorption. The peptization of hydrous oxides by caustic alkali is due to the preferential adsorption of hydroxyl ion. The water-peptized colloids like many of the organic emulsoids will peptize many precipitates, so that aside from being protective colloids they may disintegrate precipitates already formed. There may be any number of colloidal aluminas varying from anhydrous alumina, up to the most highly hydrous form that can be obtained.

Precipitates may be reverted to sols by the removal of the agglomerating agent, but this cannot take place unless it is possible to wash out the agglomerating agent.

When a sol is stabilized by the presence of an adsorbed ion the amount of an electrolyte necessary to precipitate it will vary with the nature of the cation, the anion and the dispersed phase. While it is generally true that an ion of higher valence will be adsorbed more strongly than one of lower valence there are cases where this does not apply. As Bancroft phrases it in speaking of the precipitating powers of various cations "The organic cations come in where they please and play havoc with any rule as to valency."

PHENOMENA IN WATER PURIFICATION

Alumina in filter effluents

The occurrence of alumina in some form in the effluents of mechanical filter plants is a fact that has been recognized since the early days of this type of filtration. An exhaustive study of mechanical filtration of the Ohio River water at Louisville by Fuller in 1898 brought out the following facts for that water:

1. Alum added to the raw water produced a reduction in alkalinity less than the theoretical reduction.
2. The difference between the actual and theoretical reductions increased with increasing turbidities.
3. Efficiency of filtration could not be depended upon in the absence of complete coagulation.
4. Time period for good coagulation increased with increasing turbidities.
5. Alumina was present in some form in the filter effluents and traces of dissolved alumina were found during chemical analyses of effluents.

It was believed for some years that the alum could not exist as alum in the effluent if there was alkalinity present, but more recently

in connection with the coagulation of colored waters some engineers^{4,5} have mentioned the possibility of the alum being adsorbed by the residual coloring matter in such a way that it is kept from reacting with the alkalinity present.

The writer had occasion a short time ago to study the core stain troubles in an ice plant using city water furnished from a large mechanical filter plant in which alum is used as a coagulant. The water from the mains was passed through a pressure filter containing

TABLE 1
Analyses by M. C. Whipple

	(A) WATER SUPPLIED TO PLANT FROM CITY MAINS	(B) WATER FROM PRESSURE FILTERS WITHOUT CHEMICALS	(C) MELTED CLEAR ICE	(D) WATER SUCKED FROM CORES	(E) IMPURI- TIES REMOVED BY FREEZING B-C	(F) CONCEN- TRATION OF IMPUR- ITIES IN THE CORE WATER D/E
Color.....	10.0	7.0	1.0	31.0	6.0	5.1
Residue total.....	67.0	64.0	20.0	478.0	44.0	10.9
Loss on ignition.....	20.0	17.0	8.0	84.0	9	9.4
Albuminoid ammonia...	0.028	0.028	0.000	0.202	0.028	7.2
Nitrites.....	0.002	0.001	0.002	0.005	-0.001	
Nitrates.....	0.450	0.45	0.00	1.50	0.45	3.3
Oxygen consumed.....	2.3	1.7	0.6	7.7	0.9	8.5
Chlorine.....	5.0	5.0	1.5	53.5	3.5	15.3
Total hardness.....	28.5	28.5	0.0	172.0	28.5	5.9
Alkalinity.....	11.5	11.5	1.0	89.0	10.5	8.5
Incrustants.....	17.0	17.0	0.0	83.0	17.0	4.9
Suspended iron.....	0.05	0.0	0.0	0.45	0.0	} 5.0
Iron in solution.....	0.10	0.10	0.0	0.05	0.10	

sand and several layers of felt, no chemicals were applied. From this filter it passed through a cooling tank into the ice containers in a cold brine bath. During freezing the water was kept agitated by cold air injected into the bottom of the container the bubbles rising through the liquid. Freezing worked inward from the sides and bottom of the container, crystals of pure ice forming until the bulk of the impurities in the water supplied to the container were concentrated in the unfrozen core. This core water was dark colored and dirty and in general practice was sucked out before the completion of the freezing process and the core was refilled with water from the

⁴ Whipple, Hot Water Troubles, Journal, Proc., 1911, p. 267.

⁵ Hazen, Clean Water and How to Get It.

cooling tank. Table 1 gives the analyses of the water as it comes from the mains, the effluent of the pressure filter, the melted clear ice and the dirty water sucked from the core and the concentrations of the impurities in the core water. The variations in concentrations are due to the precipitation of some impurities during freezing and to adhesion to the core walls.

The logwood test which is sensitive to one part in ten million gave only a trace of alumina in the water from the mains but showed 2 grains per gallon figured as aluminum sulphate present in the core water. Now if the concentration of aluminum sulphate was in the same proportion as the concentration of total residue or chlorine the presence of 0.18 or 0.13 grains per gallon of alumina figured as aluminum sulphate was indicated in the effluent of the pressure filter.

A sample of wash water from the pressure filter was collected in a bottle and allowed to stand for several days. A heavy brown gelatinous precipitate settled to the bottom of the bottle and when the cork was removed a strong odor of hydrogen sulphide was given off. This sediment, consisting of alumina and organic matter in a state of slow decomposition, represented the concentration of the impurities extracted from the tap water by the pressure filter. But the impurities removed were only three parts per million of color and residue lost on ignition and 0.05 part per million of iron the amount that was present in suspension in the tap water. The oxygen consumed was reduced by a little more than one quarter. The impurities passing the filter as listed in column "B," table 1, were partly in solution, partly in the form of organic sols and perhaps partly in the form of suspensoids. Under these conditions the question may be raised as to the condition of the alumina that passed through the pressure filter. Is it not probable that the alumina which was present as a trace in the tap water as indicated by the logwood test was present as hydrate, which either had passed through the city filters or was formed in the mains and that it was this hydrate together with some agglomerated organic matter that was removed by the pressure filter? What then of the alumina that passed on and was present in such appreciable quantities in the core water? This might have been present as a solution of sulphate within the organic sols and as a colloidal suspension of alumina surrounded and protected by organic sols. Under these conditions the logwood test would not necessarily detect it. The subsequent process of aeration, freezing and the resulting concentrations would destroy the sols to a certain extent

releasing hydrate or allowing sulphate to react with alkalinity, so that the relatively high concentration of alumina in the core water of two grains per gallon could be detected by the logwood test.

It is unfortunate that these investigations were not quantitative as well as qualitative in character as they probably would have given still more interesting results. Ice plants using city water supplies are quite common and should offer an excellent field for investigations of impurities in various tap waters.⁶

Howard and Hannan⁷ working in the Toronto Filtration Plant Laboratories have recently made extensive investigations of natural waters treated with alum to determine the presence of alumina in the filter effluent. They were unable to find a water which after treatment did not yield a positive alumina reaction, but their work has not progressed far enough to determine definitely the form of the residual alumina.

It does not seem necessary to give more space to the discussion of alumina in filter effluents, where treatment with alum is part of the process of purification, as it is almost universally accepted as a fact and has been demonstrated quite generally, but the form in which this alumina passes the filters is still a mystery. The form probably varies with the kind of impurities present both in the water and in the commercial alum used, so that a careful determination of the residual impurities in the treatment of a given water will not apply to another water or even to a water from the same source under different conditions.

RELATION OF COLOR AND ALKALINITY TO COAGULATION

Attempts have been made to formulate the quantity of alum required for good coagulation in treating a colored water when the color and alkalinity (titration with methyl orange) are known. These have proved fairly approximate when the water is drawn from a source free from sewage pollution, in which case the colloids present are products of decomposition of organic matter on the particular drainage area in question. A catchment area which does not undergo a marked change from year to year will produce similar colloids during corresponding seasons in the water which runs from it. On the other hand a river which receives the raw sewage of cities and

⁶ Joseph Race, in studying treatment of colored water, made use of ice plant core water in Ottawa, Ontario.

⁷ The Canadian Engineer, May 13, 1920.

wastes of industrial plants will show high concentrations of various complex sols during periods of low runoff that will vary from hour to hour in nature and in concentration and play havoc with any general formula for alum required for good coagulation.

On figure 1 are plotted the results of bottle coagulating experiments carried out through a period of several years on raw water from a small stream unpolluted by sewage and draining an area which is largely wooded and on which there is a small scattered rural population. The color and alkalinity of the water was noted each day and a series of bottles of this water were dosed with varying rates of alum and the lowest dose giving good coagulation was

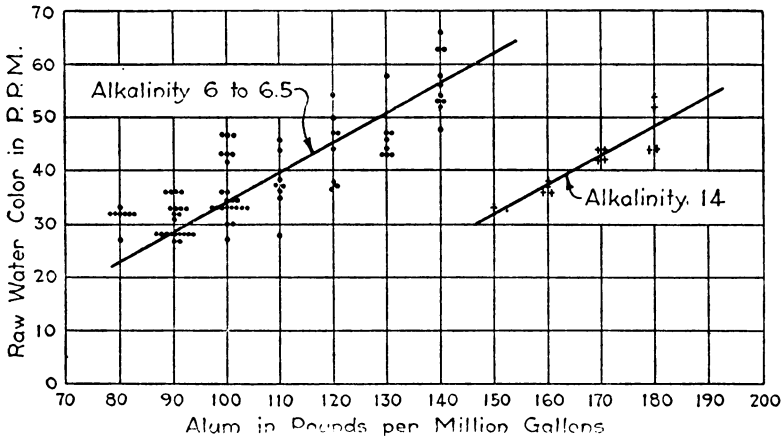


FIG. 1. ALUM REQUIRED FOR GOOD COAGULATION IN A WATER CONTAINING NO SEWAGE AND ONLY SLIGHT POLLUTION FROM SMALL RURAL POPULATION

recorded. By picking out the experiments when the alkalinity was from 6 to 6.5 p.p.m. and plotting the points with pounds of alum per million gallons as abscissas and color as ordinates a group of points was obtained approximated by a straight line giving 92 pounds per million gallons for a color of 30 and 129 pounds per million gallons for a color of 50. Points plotted when the alkalinity was 14 p.p.m. gave another group, again approximated by a straight line giving 147 lbs. per million gallons for a color of 30 and 183 lbs. per million gallons for a color of 50. Points plotted for alkalinities between these limits were approximated by similar lines lying between these two lines in the order of the alkalinities. From these curves it

will be seen that the alum required for good coagulation of this particular water varies in a general way directly as the color and directly as the alkalinity and that the curves may be used to give a fair approximation of the alum required when the alkalinity and the color are known.

The writer endeavored to work out similar curves for a colored river water which contained the raw sewage of several towns and the wastes of a number of large paper mills. The plottings were most discouraging and gave little more than a scattered mass of points although lines drawn through the centers of gravity of groups of the points fell in positions similar to those drawn on figure 1. But such lines would not give even a fair approximation of the alum dose required for good coagulation based on color and alkalinity alone. It was obvious that other conditions existed in this water which were more controlling than the color or alkalinity as determined according to standard methods. Titration with methyl orange does not give the true alkalinity of this water. It was found that hydrogen peroxide added to the water and heated to release the oxygen caused reduction in the apparent alkalinity of more than 25 per cent at times and it may be that this oxidizable organic matter formerly absorbed the acid of titration giving fictitiously high alkalinity results.

FLOW OF RIVER CONTROLLING FACTOR IN ALUM REQUIRED FOR GOOD COAGULATION

In studying the operation of a mechanical filter plant treating this particular river water it was observed that a high dose of alum was required at times of low flow regardless of the color and alkalinity of the water. This was true for the low flows in winter as well as for the low flows in summer and, therefore, could not be attributed to temperature conditions. A reduction in color of from 80 per cent to 90 per cent was found to result from good coagulation and that while this could be attained with less than 200 lbs. per million gallons of alum during periods of high runoff, doses of from 400 to 500 lbs. per million gallons were required at times of minimum runoff. This was true for low flow colors and alkalinities approximately the same as those during high flows, although the average colors during high flows were somewhat lower than the average colors during low flows. Taking all of these observations into consideration it was considered best to show the percent

color reduction for each unit of alum used for all records of operation lying within given average flows of the river. Figure 2 gives the averages of all months falling within each 1000 cubic feet per second interval of flow. The flows of the river are plotted as abscissas and the percent reductions in color for each 100 pounds per million gallons of alum used are plotted as ordinates. The record covers thirteen years. It will be seen that the average of all months including both winter and summer months, in which the flow of the river was less than 1000 second feet, gives a reduction in color of only

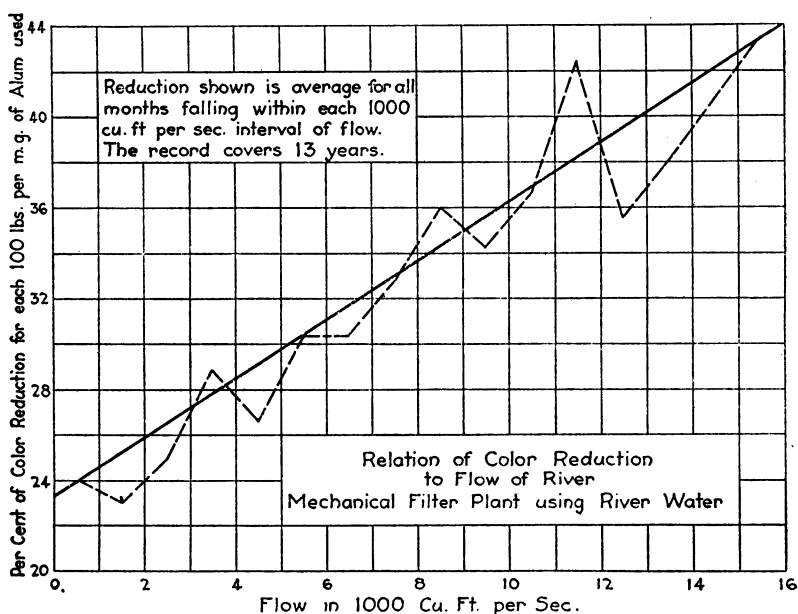


FIG. 2

24 per cent for each 100 pounds per million gallons of alum while the average of all months during which the flow was between 15,000 and 16,000 second feet gives a reduction of 43 per cent. Thus the amount of alum required to produce good coagulation of this river water is inversely proportional to the flow of the river.

Figure 3 is self-explanatory as the curve is plotted in a similar manner to that on figure 2. It shows that the bacterial efficiency of the filters decreases as the flow of the river decreases and this is due to the limitations of the various parts of the plant, and to the greater tendency to underdose the water when a high dose is required. The

coagulation basins hold a four hours supply and the highest consumption took place at times of minimum river flow thereby reducing the period of coagulation below what it was at times of high river flows. The time factor is important for good coagulation and the time required increases as the alum required increases. Hence the low bacterial efficiencies at times of low flow were due primarily to an insufficient period of coagulation and secondarily to insufficient alum being applied at certain times. This tendency for incomplete coagulation to carry bacteria through filters has been generally recognized and it is an element of danger in the treatment of polluted waters. The importance of securing a sufficient dose of alum and a sufficient period, for coagulation before filtration cannot be over emphasized.

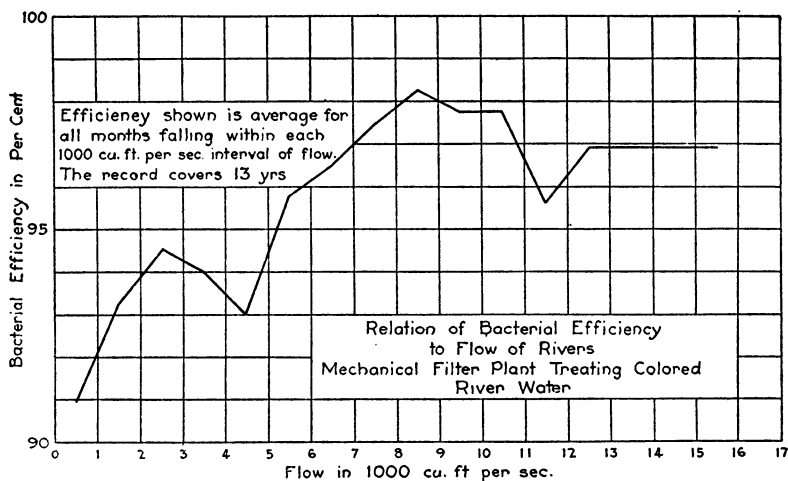


FIG. 3

Many experiments were conducted to determine the effect of soda and lime on this water added before and after application of alum added to the filter effluent and to coagulated water containing floc. In every case the color was increased. Floc sometimes formed and precipitated when alkalinity was added to the filter effluent which was alkaline to methyl orange by no less than 5 p.p.m. When the alkalinity was added before the alum more alum was required to cause precipitation, when added after the alum the precipitate went partly or entirely back into solution depending upon the alum dose, but the worst results of all were obtained in treating wash water with lime water. The high addition of alkalinity increased the color of the wash water to seven times its original color.

It has been noticed in studying the coagulation of several waters, both those containing emulsoids and those containing suspensoids, that untreated raw water admitted to a basin containing floc produced by former alum treatment will redissolve some floc. In the case of colored waters, colors may result one half again as high as the raw water color. This phenomenon causes a good deal of trouble in the operation of coagulation basins in many localities. Carelessness of the operators in allowing the coagulant to underfeed or to run out entirely or breakdowns in the apparatus may spoil the water in a large basin for hours.

There is perfect accord between all these phenomena and the observations of colloid chemistry. Alkalinity increases the color because it peptizes the emulsoids increasing the total surfaces. With the increase in surfaces there is greater adsorption for the coagulant applied and more is required to satisfy this adsorption. In the case of the relatively small unpolluted stream, the nature of the emulsoids is more or less constant throughout a term of years, as their points of origin are similar from year to year. There is then a direct relation for waters of this type between the coagulant required for good coagulation and the color and alkalinity of the water. But in the case of the polluted river water at times of low runoff, the rapidly varying concentrations of sewage and industrial wastes is responsible for great and sudden changes in the kinds and numbers of colloids present in the water. Alkalinity determinations will not give a reasonable indication of the relative alkalinities from hour to hour, because certain colloids prevailing at one moment will adsorb more of the acid of titration than certain others prevailing the next. The relative adsorptions for the coagulant will vary at the same time, so that no relation can be found between the alum required and color and alkalinity for a water of this type. In these circumstances it is not surprising to find a direct relation between the flow of the river and the alum required for good coagulation. The low river flows are made up of water highly charged with the organic wastes of man while these are greatly diluted during the higher river flows. A sudden flood flow, however, after a long period of low runoff may carry large percentages of these organic wastes for a short time due to the scouring out of the river bottom where considerable sludge had deposited when the velocity of flow was low.

The formation of floc when a small quantity of alkalinity was added to an alkaline effluent of a mechanical filter plant can be explained if

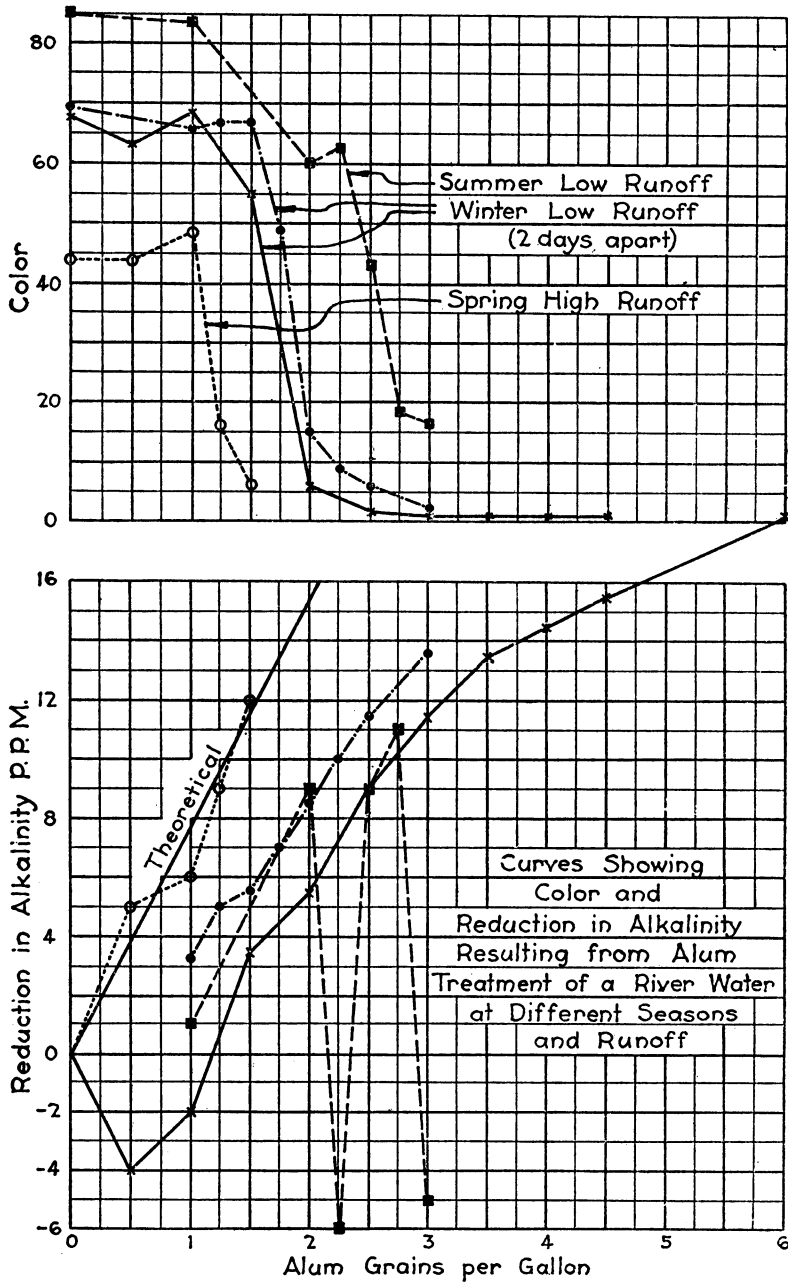
it is assumed that the emulsoids responsible for the residual color contain dissolved aluminum sulphate. The alkalinity added is adsorbed by the emulsoids whereupon reaction between the alkalinity and the adsorbed alum takes place forming aluminum hydrate and reducing the alkali present so that peptization does not take place. Experiments carried out by the writer have shown both reduction in alkalinity and color to result from the addition of small amounts of lime to a filter effluent that was alkaline to methyl orange and these results were accompanied by the formation of floc which settled. Higher doses of lime peptized the floc and color increasing the latter materially. This is exactly what happened when concentrated lime solution was added to filter wash water and is a case of peptization by an alkali.

The peptization of precipitated floc in coagulation basins by raw water or under dosed water may be due partly to washing out of the precipitating agents but is probably caused to a greater extent by adsorption of the colloids and alkalinity in the entering water.

THEORETICAL AND ACTUAL REDUCTION IN ALKALINITY DUE TO ALUM APPLIED

When titration with methyl orange is used to determine alkalinity, the actual reduction in alkalinity when alum is added to a colored water is often less than the theoretical reduction, sometimes approximately the same and in a few cases greater than the theoretical. In other words, there is no direct relation between the reduction in alkalinity as commonly determined and the application of alum to some waters. This means that one or both of two things occur, namely, direct action between the alum and colloidal matter present or between these colloids and the acid used in titration. As a matter of fact the color is reduced when the acid is added showing that some such action takes place between the color and acid of titration.

Bottle experiments were conducted with raw water from the same polluted river that we have been discussing to show the color removal corresponding to the alkalinity reductions with various amounts of alum. Alum was added in varying quantities to a series of bottles of raw river water and after four hours the water was filtered through paper and the colors and alkalinities of each determined. Typical results of four such tests are plotted in figure 4. One test was made on water collected during low runoff in the summer, two tests two days apart during low winter runoff and one test during spring high



runoff. The colors and reductions in alkalinity are plotted corresponding to the alum doses applied in grains per gallon, and the theoretical reduction in alkalinity is shown for comparison. No marked color reduction was found in any case until a dose of at least one grain per gallon of alum was reached. Up to the point where color removal began, with the exception of the high runoff water, the reduction in alkalinity varied up and down below the theoretical and in one case an apparent increase of 4 p.p.m. in alkalinity was recorded for a dose of $\frac{1}{2}$ grain per gallon of alum. While the color removal is going on the alkalinity reductions approximate the theoretical as shown by the slopes of the alkalinity reduction curves but in the case of the summer low runoff water the alkalinity jumped up and down to a surprising degree. It is interesting to note, however, that between one and two grains of alum the alkalinity reduction was about parallel to the theoretical during a primary reduction in color; then between 2 and $2\frac{1}{4}$ grains the color increased and the alkalinity reduction went down to -6, between $2\frac{1}{4}$ and $2\frac{1}{2}$ grains it went back to 9 corresponding to a secondary rapid reduction in color. The alkalinity reduction was about parallel to the theoretical between $2\frac{1}{2}$ and $2\frac{3}{4}$ grains while the rapid reduction in color continued and then jumped to -5 as the color curve flattened out to a residual color of 16.

The actual reduction in alkalinity for the high runoff water approximated the theoretical, although the slope is considerably steeper during the period of color removal.

All of these results were obtained on water from the same source of supply and show how futile it is to outline a standard method of treatment at any time. In the actual operation of the filtration plant it has been found necessary to change the alum dose from hour to hour as rapid changes in the nature of the raw water have occurred, making a dose which was sufficient for good coagulation during one hour insufficient for dosing the water encountered in the next hour.

A plausible explanation of the experiments recorded in figure 4 can be given, if we assume that the organic matter present soaks up the titration acid or the aluminum sulphate to a definite concentration and any acid or sulphate present in excess of this concentration reacts with the alkalinity. Titration then shows higher alkalinities than are actually present. The alum in excess of that absorbed by the organic matter reacts with alkalinity present forming hydrate of alumina which coats the colloidal organic matter causing agglomera-

tion and precipitation. If either the alum or the alkalinity are insufficient to produce sufficient hydrate to coat all of the colloidal organic matter some of it will remain dispersed in the liquid and pass the filters containing the dissolved alum and a partial coating of hydrate. This partial coating of hydrate would give a positive test with logwood, but the contained aluminum sulphate would not be indicated unless the colloids were broken up or some agent added which would be absorbed by the colloids strongly enough to displace the aluminum sulphate.

The abnormal results on the sample of water collected during low summer flow may have been due to a variety of colloids, some acting as protective colloids for others and the protective powers may have been broken down or reversed by the increasing concentrations of alum. If reversal of protective action took place the colloid formerly protected would become exposed and might have greater adsorption for alum than those formerly exposed. In the same way they would adsorb the acid of titration and increase the apparent alkalinity. The colloids responsible for a residual color of 16 after a dose of 3 grains per gallon of alum must have a large capacity for adsorbing sulphuric acid to exhibit an apparent alkalinity of five parts per million in excess of the alkalinity of the undosed raw water.

At first glance the reduction in alkalinity curve for the spring high runoff sample would indicate a reaction of true solutions, but the color curve is similar to the others. Here also there was something going on between the color and alum up to a dose of 1 grain. There was probably fictitious alkalinity in this case but in such amount as to be equal to the alkalinity reduction that should have resulted from a dose of 1 grain of alum. This amount of alum when adsorbed by the color probably satisfied its power of adsorption for acid and the apparent reduction in alkalinity corresponded to the theoretical. Later when the color was being removed and the alkalinity reduction was greater than the theoretical it is possible that some of the adsorbed alum was released and reacted with alkalinity to aid in the color removal. This would account for an actual reduction in alkalinity greater than the theoretical.

Similar phenomena to those described have been noted in studying several colored waters and curves similar to those in figure 4 could be drawn to show the coagulation experiments conducted with them. Four curves all for the same river were selected to show how the nature of a polluted source of supply may vary according to the con-

centration of the polluting matter and not because this water is different from that that may be found somewhere else.

Major J. Morison^{*} in studying a turbid water in India found different optimum doses of alum that would give good coagulation and that between these doses was a point where no coagulation resulted. The experiments to determine the precipitating powers of alum on a colloidal solution of mastic mentioned under the head of "Facts from Applied Colloid Chemistry" may shed light on this phenomenon. The first optimum dose probably caused coagulation by adsorbed hydrous alumina and between this and the second optimum dose peptization was caused by the hydrolyzed colloidal alumina. The coagulation resulting from the second optimum dose of alum may have been due to the adsorbed sulphate ions as in the case of the mastic.

It is interesting to note that Morison found difficulty in coagulating this water when organic matter was present in it at certain seasons, this being due without doubt to the protective emulsoids. He calls attention also to the peptization of floc when raw water is brought into contact with it.

NATURE OF ALUMINA IN FILTER EFFLUENTS

It is reasonably certain that alumina may exist in any number of colloidal forms in the effluents from filter plants using alum treatment as part of the process of purification. The course of the reaction when natural waters are treated with alum leads us to believe that filter effluents containing emulsoids either alone or as protective colloids peptizing suspensoids contain undecomposed alum even when the water is alkaline. It seems reasonable to suspect the presence of many different combinations of colloids such as emulsoids alone containing dissolved alum; emulsoids acting as protective colloids for natural suspensoids present or for alumina varying from anhydrous alumina up to highly hydrous forms; then there is the possibility of the emulsoids alone or acting as protective colloids being partly coated by adsorbed alumina in concentrations which were insufficient to cause agglomeration before filtration. In all cases there is the possibility of undecomposed alum dissolved in the emulsoids. If such mixed up systems occur they are certainly in an unstable state and will break up wholly or in part when other elements are intro-

^{*} Indian Journal of Medical Research, April, 1916.

duced to the solution or upon the application of heat. Thus when water enters iron pipes some of the colloids will be adsorbed by the iron when reaction between them and the iron may take place. Heat applied in hot water boilers may cause changes that result in agglomeration and precipitation of some of the colloids and acid released to attack the iron of the hot water backs and pipes and discolor the precipitate. A precipitate will be cumulative so long as the velocities through the boiler are low and will be discharged as dirty red water when a heavy draft takes place.

INCREASE IN BACTERIA SUBSEQUENT TO PURIFICATION

No phenomenon connected with water purification has caused more concern and in a few instances alarm than that of the apparent return to life of the bacteria between the clear well and the consumers. This was almost universally recognized before the introduction of chlorine treatment and has continued although not so marked since chlorination has become general as a final safe guard in water purification. Cases are on record where chlorine was added in considerable quantities to the water entering the filtered water reservoir where the bacteria were practically reduced to zero and samples taken from the taps showed relatively high counts and the presence of *B. coli* in 10 cc. when negative results were obtained at the plant.

It does not seem such a great step in reasoning by analogy from Bechhold's assumption, that suspensoids adsorb emulsoids and are protected by them, to assume that certain of the smaller bacteria also adsorb emulsoids and are protected by them. If bacteria adsorb organic colloids to form a coating of the organic sols about them the phenomena of increase in numbers after purification and the variable longevity of *B. coli* and *B. typhosus* in different waters can be explained. Both of these bacteria enter the water in intimate connection with the organic wastes of animal systems, and part of these wastes are peptized by the water into sols. If the colloids that are adsorbed by the bacteria contain the necessary ingredients to keep them alive they will persist in living beyond the period that the same bacteria can exist in pure water. It is reasonable to suppose that the colloids do contain this food as they are from the same source as the bacteria.

It has already been pointed out that the sols of sewage pollution are the most difficult to treat satisfactorily. It is therefore probable that the percentage of these to the total sols present is greater in the

filter effluent than it was in the raw water. If this is true there may be considerable organic matter of sewage origin in the effluent of a plant treating polluted water when the residual color is high or when there is an insufficient dose of alum applied. Bacteria may be surrounded and protected by the emulsoids present in such a way that they will not start colonies on a gelatine plate inside of 48 hours and so that the chlorine if applied to the water will be adsorbed by the colloids until there is not enough free chlorine left to destroy the bacteria when they are released. These suppositions offer possible explanations of the increase in bacteria between the plant and the consumer and if they are true the subject is one for careful and immediate study.

SUMMARY

The writer does not wish to convey the impression that he is satisfied that the various theories set forth in this paper are true explanations of the phenomena discussed. The purpose of the paper is to compare observed phenomena in water purification with those in colloid chemistry, and to suggest explanations of the former based on experimental proofs and reasonable assumptions developed in the latter.

It is clear that there is an application of colloid chemistry to the study of filtration, but the phenomena in water purification cannot be explained satisfactorily until many investigators have made careful studies of a large number of different waters, and until their results have been compared.

The following is a summary of the main points:

1. When alum is used as a coagulant in the process of water purification, alumina is always present in some form in the effluent of the plant.
2. Increasing turbidities call for higher doses of alum for good coagulation; and when organic matter is present also in appreciable concentrations, still more alum is required to produce a good precipitate.
3. When soft colored water is obtained without storage from a catchment area practically free from pollution, there is a direct relation between the alum required for good coagulation and the color and alkalinity (determined by titration with methyl orange). In this case, when the alkalinity remains the same, the alum required is directly proportional to the color; and for a given color the alum

required is directly proportional to the alkalinity. This is true within certain limits, as there are slight variations in the nature of the organic matter at different seasons of the year, or due to unusual conditions on the catchment area, which will cause a certain variation above or below the average conditions.

4. The water from a river receiving pollution from sewage and industrial plants fails to show even a fairly approximate relation between the alum required for good coagulation and its color and alkalinity. In this case there seems to be a relation between the concentration of pollution and the amount of alum required. Thus, when the runoff is low and the percentage of pollution is high, large quantities of alum are required regardless of the color and apparent alkalinity; and when the runoff is high good coagulation can be obtained with relatively small quantities of alum. This would not be true of a river carrying considerable turbidity during high runoff, as the turbidity itself would call for extra alum.

5. When alum is added to turbid or colored waters the reduction in alkalinity does not correspond to the theoretical reduction. In a colored water there seems to be first a direct action between the organic matter and the alum up to a definite concentration of the alum; and while this is going on there are apparent changes in alkalinity which differ considerably from the theoretical, and very little change in the color. Between alum doses where coagulation and color removal begin and end, the reduction in alkalinity corresponds very closely to the theoretical.

6. When turbidity or coloring matter in considerable quantities passes through the filters, due to absence of coagulation or to insufficient dose of coagulant, bacteria also pass through and reduce the bacterial efficiency of the plant before the application of chlorine; and when these conditions exist heavier doses of chlorine are required to produce sterile plates, or to cause a positive starch iodide test, than are required when the effluent is clear and practically colorless.

7. Increase in bacteria subsequent to purification has been generally recognized, although it occurred to a greater degree before the use of chlorine became general. This phenomenon is recorded, however, in cases where chlorine is used, and it is a common occurrence to find relatively large numbers of bacteria and positive *B. coli* tests in some tap waters when 48-hour plates taken at the plant are practically sterile and *B. coli* tests are negative.

1a. Commercial alum is not a pure chemical, and it is added to waters containing impurities, some in solution, some in suspension, and the rest in the form of sols, both suspensoids and emulsoids. If these impurities do not exist in the water, the commercial alum will supply some of them when it is added. Upon the application of alum to water some of the aluminum sulphate may be hydrolized to alumina and sulphuric acid, and some will react with the alkalinity to form hydrate. The alumina may be in any number of colloid forms, varying from anhydrous alumina to the highest possible hydrous forms. Here we have a complicated system of colloids, in which adsorption plays a major part, and selective adsorption is probably responsible for the variations recorded in treating different waters containing different kinds of sols. When emulsoids are present, some soluble aluminum sulphate may be adsorbed out of the water and dissolved in the emulsoids. Then alumina may be adsorbed, forming gelatinous coatings on the surfaces of the emulsoids; or some of the emulsoids may be adsorbed by the colloidal alumina or other suspensoids present, thereby incasing some of the alumina, after which hydrous alumina may be adsorbed by the system, until agglomeration and precipitation occur. If either the alkalinity or alum is insufficient to produce enough hydrate to cause complete agglomeration and precipitation of all the sols present, some of them remain in the colloidal state and pass through the filters. The residual sols will be complex in character and it is possible that they may contain alumina in such a way that all of it will not be detected by the logwood test. That is, colloidal alumina may be surrounded and protected by adsorbed emulsoids in which some aluminum sulphate is dissolved, but on the exposed surfaces of the emulsoids there may be some adsorbed hydrate, although not enough to cause agglomeration, and the presence of this would be indicated by the logwood test, while the protected alumina and the alum dissolved in the emulsoids would not be indicated until something caused the decomposition of the system. Therefore, it is probable that alumina and aluminum sulphate may be present undetected in filter effluents when colloidal organic matter is present.

2a. Increasing turbidities require increasing doses of alum for good coagulation, because the total surfaces which adsorb the hydrate are greater and must be coated before agglomeration will take place. When organic matter is present the emulsoids may adsorb part of the alum, and until this adsorption is satisfied, sufficient hydrate will not be formed to cause agglomeration.

3a. The emulsoids present in a soft, colored water practically free from pollution are similar in nature from year to year, provided they are not changed by storage or radical differences in conditions on the catchment area. For a given alkalinity the total surfaces of the organic sols present are probably directly proportional to the color, and therefore a proportional amount of alum is required to satisfy the adsorption of the sulphate by the emulsoids, and to produce sufficient hydrate to coat the surfaces and cause agglomeration. For higher alkalinity the emulsoids are probably peptized to a greater degree, thereby having larger total surfaces for a given color and consequently requiring more alum for precipitation.

4a. The emulsoids present in a polluted stream are very complex in nature, and may vary considerably from hour to hour. Some of them will have greater adsorption for sulphate and hydrate than others, and there will be no direct relation between the color and the total surfaces, because sols of one kind may have greater surfaces for a given color than sols of another kind, and some of them may have no color at all.

5a. Alkalinity determined by titration is not true alkalinity. The acid of titration is adsorbed by sols present in the water before the reaction between the acid and the true alkalinity can be completed. Thus titration gives higher than true values for alkalinity in alkaline waters. In the same way alum applied may be adsorbed by sols, and when emulsoids are present the sulphate may be dissolved in the emulsoids. When this adsorption is satisfied, reaction between the alum and alkalinity may take place, producing hydrate which is adsorbed by the sols, causing agglomeration and precipitation. During this action the reduction in alkalinity should approximate the theoretical.

6a. Bechhold's assumption that emulsoids are adsorbed by suspensoids to cause a protective coating of emulsoids about the suspensoids may apply to the phenomenon of reduced bacterial efficiency of filters when colloidal matter passes through. If we assume that bacteria may be protected in a similar manner to suspensoids, it is clear that they will not be adsorbed by the sand if the colloids surrounding them pass through.

7a. If colloids can be adsorbed by bacteria to form a protective coating about them, it may be that some bacteria are kept from starting colonies on gelatine plates within a 48-hour period of incubation. Also it may be that these colloids will adsorb all of the chlorine

used in the final treatment of a filtered water, so that when the water enters the distribution system where other conditions exist, and some of the protective colloids are broken down releasing the bacteria, the water will show apparent increases in bacteria and the presence of *B. coli* when the standard tests of the effluent of the filters showed the water to be beyond reproach.

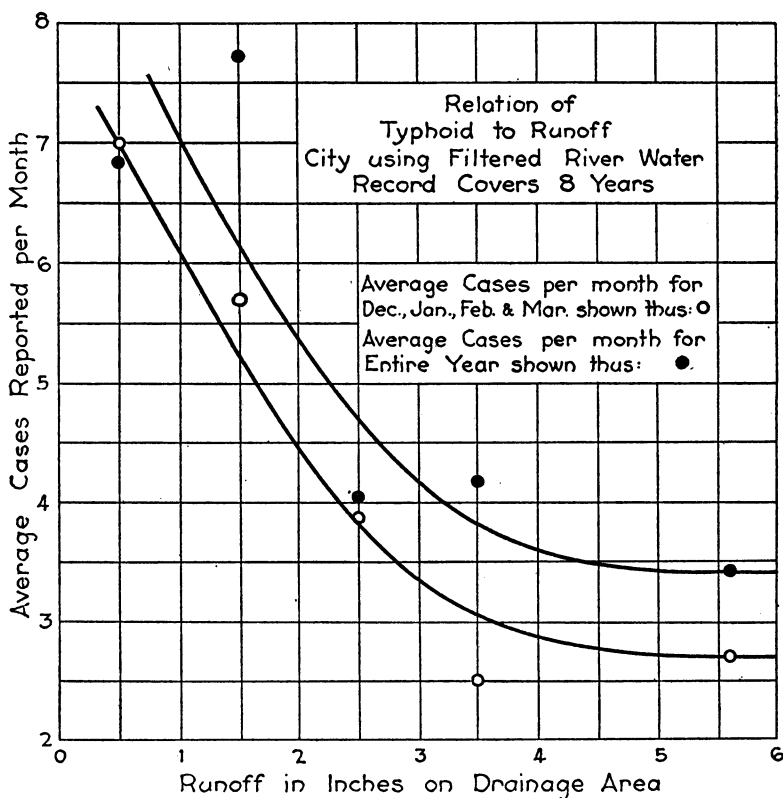


FIG. 5

Everyone knows that the introduction of filters for the purification of water supplies from polluted sources greatly reduced the morbidity and deaths from water borne diseases. It is true also that the more recent use of chlorine as a final treatment applied to the effluents of many filter plants has further reduced and in some cases almost eliminated these diseases, but can we now assume that the present methods of purification have eliminated all possibility of

infection? Or, is it more reasonable to suspect that some typhoid and other related diseases may be caused by filtered water supplies especially when *B. coli* are consistently found in the tap water? Some colloidal matter passes through filters and often when the colloids are present in the effluent in considerable amounts the bacterial efficiency is reduced. Is it not probable that with even fewer colloids present in the effluent, if they are of a certain nature, some bacteria are also present and may be surrounded by the colloids in

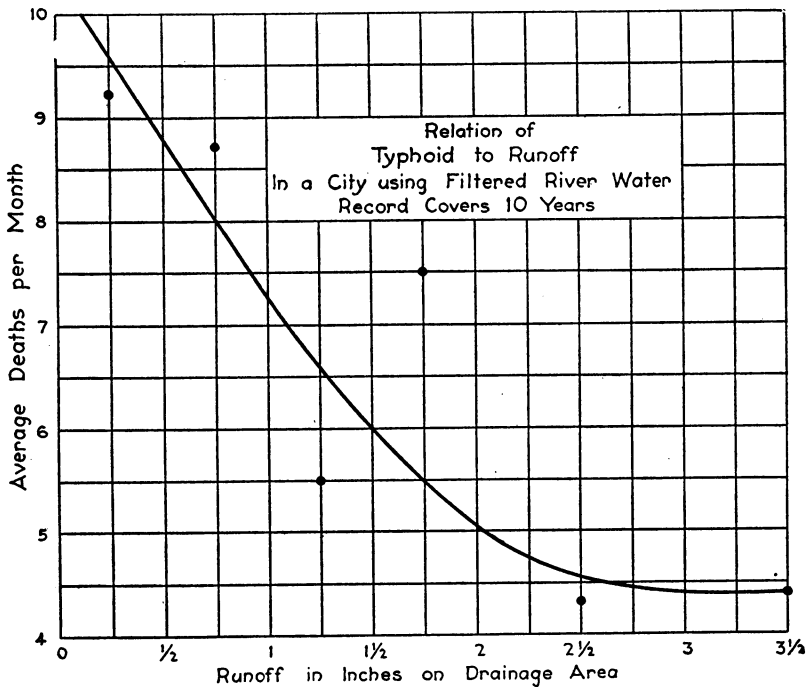


FIG. 6

such a way that they will not start colonies on gelatine plates to indicate their presence? Then if the supply is from a river which receives sewage above the intake is it not possible that the relatively high concentrations of pollution at times of low runoff may cause colloids and bacteria of sewage origin to be present in the effluent?

With these questions in mind the writer studied the statistics of two cities both taking water from polluted rivers, one purified by slow sand filters and the other by mechanical filters. The typhoid was compared with the runoff over periods of several years and the

cases of deaths per month were summed up for different intervals of runoff and plotted as average cases or deaths per month in the middle of the intervals of flow selected. These results are plotted in figures 5 and 6.

In order to show that the relation between typhoid and runoff was similar during the winter months to the relation for the entire year a curve was plotted on figure 5, giving the average typhoid cases per month for different intervals of runoff for the months of December, January, February and March. These curves indicate that the typhoid, while low for the year as a whole, is relatively high during periods of low runoff and relatively low during periods of high runoff. It must be borne in mind that these curves simply represent the statistics for two different cities and plants and therefore prove nothing. They are given to suggest a method of investigation that may be followed in studying conditions throughout the country, in the hope that many plant operators will be interested sufficiently to study the statistics for their plants. Meanwhile there are certain precautionary measures that can be taken to guard against danger of infection from water supplies during periods of low runoff, or other conditions which may cause concentration of pollution in the raw water at certain times.

Precautionary measures

It is certain that organic sols are present in the effluents of many filter plants treating water from polluted sources and it is probable that some of these sols are of sewage origin. If it is possible that some of the sols act as protective colloids for bacteria and thereby carry them through the purification process alive, it is advisable to reduce colloidal matter in the filtered water to a minimum at all times and especially during periods of low runoff when the concentration of pollution is high. This can be done in most cases by the proper chemical treatment supplemented by a coagulation period sufficient to allow the reactions to be completed before the water enters the filters. In many plants the presence of considerable colloidal matter in the effluent is permitted during low river flows in order to reduce the consumption of alum, and if coagulation is continued throughout the year, as it is necessarily carried out during turbid flows, the effluent can be made relatively free from organic sols at all times. It would seem to be advisable to do this in all plants treating polluted waters until it has been proved whether or

not colloids can be responsible for carrying disease germs through our lines of defense against them.

There may be a question raised as to sewage treatment at points above a given water supply and, if chemical treatment is resorted to, care should be taken that the chemicals used do not peptize the organic matter present. Such chemicals will remove the nuisance of odor from sewage by arresting decomposition, but they may increase the danger of infection by stabilizing the organic solids so that they can proceed unchanged in the water for a long time.

The use of chlorine as a final safeguard is advisable at all times. When the amount of colloids present is low this may be entirely effective in removing the last chance of infection, but where the colloids are considerable the required dose of chlorine for immunity is uncertain. In such cases it is best to add enough to give a positive starch iodide test and probably does not need to be enough to cause a taste in the water drawn from the taps.

It is impossible for any one investigator to draw general conclusions for all waters based upon careful studies of a few supplies, because the nature and kinds of impurities present in waters are as various as the sources themselves. The subject of water purification needs the careful study and coöperation of chemists, engineers and operators so that the best method of treating a given supply can be worked out in advance of the design of the plant. The plant when built should then be capable of being operated to produce the desired results. The importance of colloid chemistry in this connection cannot be over estimated. It is hoped that some of the most noted chemists in this special field will give their attention to the colloid in its relation to water purification.